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Analysis of temperature dependence of interionic separation and bulk modulus for alkali halides

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Abstract : A thermodynamic analysis of Anderson-Grüneisen parameter is found to yield useful relations for estimating the temperature dependence of interionic separation $r(T)$ and bulk modulus $B_T(T)$. These relations can be used to predict $r(T)$ and $B_T(T)$ upto melting temperature of eight alkali halide solids. The results are compared with the available experimental data and are discussed in the view of recent research in the field of high temperature physics

Keywords : Thermodynamic properties, equations-of-state, inorganic compounds.

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1. Introduction

Various efforts have been made to understand the thermodynamic properties of solids or materials under the effect of high temperature by many workers [1–10]. In previous studies, the temperature dependence of the thermodynamic properties, *viz.*, temperature dependence of interionic separations, bulk modulus and cubical thermal expansion of solids from static lattice to the melting temperature have been studied and discussed by various expressions developed on the thermodynamic approximations and best fit relations [5,9,10]. Kwon *et al* [11] have investigated the thermal properties of KCl by using modified Einstein model. Such study required appropriate form of potential energy and huge computation. The adequate knowledge of temperature dependence of bulk modulus is very necessary for understanding the thermoelastic and anharmonic properties of solid. The expressions for temperature dependence of interionic separation and bulk modulus have been developed with the assumption that the thermal expansion coefficient depends linearly

on temperature [9,16]. This can be justified from the work of Spetzler *et al* [12] and other workers [13,14]. The cubical thermal expansion coefficient (α) is related to the density of solids assuming that Anderson-Grüneisen parameter δ_T is independent of temperature above Debye temperature θ_D [15,16]. The validity of this assumption has been discussed in Anderson *et al* [15–20]. This assumption is widely used for predicting interionic separation of alkali halides from static lattice to melting temperature because many of them have Debye temperature θ_D near to room temperature.

The aim of present paper is to develope relations for temperature dependence of interionic separation $r(T)$ and bulk modulus $B_T(T)$ by using thermodynamic relations and under following approximations :

(a) Anderson-Grüneisen parameter δ_T remains independent of volume [17–21].

(b) Anderson-Grüneisen parameter δ_T is volume dependent [20–22].

The present paper is an effort in a such direction. The method of analysis is described in Section 2. The calculated values are compared with each other and experimental values. The results and discussions are given in Section 3.

2. Method of analysis

Anderson-Grüneisen parameter (δ_T) is very important and useful quantity for developing an understanding of anharmonic properties of ionic solids. The δ_T is defined as [23,24]

$$\delta_T = -\frac{1}{\alpha B_T}\left[\frac{dB_T}{dT}\right]_p, \tag{1}$$

where α and B_T are cubical thermal expansion coefficient and Bulk modulus, respectively. These are defined as

$$\alpha = \frac{1}{V}\left[\frac{dV}{dT}\right]_P \tag{2}$$

and

$$B_T = -\frac{1}{V}\left[\frac{dP}{dV}\right]. \tag{3}$$

The Maxwell thermodynamic relation is given as

$$B_T\left[\frac{d\alpha}{dP}\right]_T = \frac{1}{B_T}\left[\frac{dB_T}{dT}\right]_P. \tag{4}$$

using eqs. (1), (2) and (4), we get following relations :

$$\frac{d\alpha}{\alpha} = \delta_T \frac{dV}{V} \tag{5a}$$

and

$$\frac{dV}{V} = \alpha dT. \tag{5b}$$

2a. Expression for temperature dependent interionic separation [r(T)]:

Integrating eq. (5a) under approximation that δ_T is unchanged with change of volume [17–19], we get well known Anderson relation [9] as

$$\frac{\alpha}{\alpha_0} = \left[\frac{V}{V_0}\right]^{\delta_T}, \tag{6a}$$

where α_0 is the value of α at $V = V_0$. The eq. (6a) is strictly based on the assumption that δ_T is independent of volume. However, in view of recent studies [20], δ_T has been found to decrease with $n = (V/V_0)$ according to the following relation [20–22]

$$\delta_T + 1 = An, \tag{6b}$$

where A is constant for a given crystal. A is determined from the initial condition, *viz*., at $V = V_0, A = \delta_T + 1$. This relationship has been widely used. Putting eq. (6a) in eq. (5a) and integrating, we get the following relation [25,26]

$$\frac{\alpha}{\alpha_0} = \frac{V_0}{V}\exp\left[A\left(V/V_0 - 1\right)\right]. \tag{6c}$$

Now putting the value of α from eq. (6a) and (6c) in eq. (5b) and integrating, we get following relations

$$\frac{V}{V_0} = \left[1 - \delta_T \alpha_0 (T - T_0)\right]^{-\frac{1}{\delta_T}}, \tag{7a}$$

$$\frac{V}{V_0} = \left[1 - A^{-1}\left\{\ln\left(1 - A\alpha_0 (T - T_0)\right)\right\}\right]. \tag{7b}$$

In eqs. (7a) and (7b), we put $(V/V_0)\left[r[T]/r_0\right]^{1/3}$ and we get the expression for $r(T)$ under approximations :

$$r(T) = r_0\left[1 - \delta_T \alpha_0 (T - T_0)\right]^{-\frac{1}{3\delta_T}} \tag{7c}$$

and

$$r(T) = r_0\left[1 - A^{-1}\left\{\ln\left(1 - A\alpha_0 (T - T_0)\right)\right\}\right]. \tag{8}$$

2b Expression for temperature dependent bulk modulus $B_T(T)$:

Starting from the assumption that δ_T is independent of temperature (T) above Debye temperature θ_D [20] and putting the value of α from eqs. (6b) and (6c) in eq. (1), we get following forms :

$$\frac{dB_T}{B_T} \quad \frac{\delta_T \alpha_0 dT}{1 - \delta_T \alpha_0 (T - T_0)} \tag{9a}$$

and

$$\frac{dB_T}{B_T} \quad \frac{-\delta_T \alpha_0 dT}{[1 - A^{-1}\ln\{1 - A_0\alpha_0 (T - T_0)\}]\,[1 - A\alpha_0 (T - T_0)]}. \tag{9b}$$

Integrating eqs. (9a) and (9b), we get following expressions for $B_T(T)$ as :

$$B_T(T) = B_0[1-\alpha_0\delta_T(T-T_0)], \tag{10}$$

$$B_T(T) = B_0[1-A^{-1}\ln\{1-A\alpha_0(T-T_0)\}]^{-\delta_T}. \tag{11}$$

The expressions from the eqs. (7c), (8), (10) and (11) are used to compute interionic separation $r(T)$ and bulk modulus $B_T(T)$ at different temperatures *i.e.* from room temperature to melting temperature.

3. Application, results and discussion

In order to demonstrate the applicability of these expressions *i.e.* eqs. (7), (8), (10) and (11) reported here, we calculate the interionic separation $r(T)$ and bulk modulus $B_T(T)$ as a function of temperature (*i.e.*, from room temperature to melting temperature). The Debye temperature θ_D of solids considered in the present study, have values near to room temperature except for LiF. The eqs. (8) and (10) work well above Debye temperature From application point of view, we have studied only eight alkali halides with NaCl structure in present study. The values of α_0, δ_T, A and r_0 at room temperature are used as input parameters which are given in Table 1 [8,25]. We use eqs. (7) and (8) to compute interionic separation at different temperatures of these alkali halides. A comparison of the

Table 1. Values of parameters at room temperature [8,24].

Crystal	r_0 (Å)	α_0 ($10^{-4}K^{-1}$)	δ_T	A	$B_T(0)$ (10^8Pa)	T_m (K)
LiF	2.013	0.999	6.15	7 15	665	1143
NaCl	2 820	1.190	5 95	6.95	240	1050
KCl	3.146	1.110	6.29	7 29	175	1043
KBr	3 289	1.160	5.88	6 88	148	1006
KI	3.525	1 230	5 83	6 83	117	957
RbCl	3.291	1.030	6.73	7 73	156	990
RbBr	3 445	1.080	6.64	7.74	132	950
RbI	3.668	1.230	6.53	7 53	105	913

calculated values and the exprimental data [5,26] of $r(T)$ at different temperatures (upto melting temperatures) is given in Table 2(a–d) along with experimental data [5,25] for the sake of comparison. It is clear from the calculated values of $r(T)$ that the calculated values of $r(T)$ of all the eight alkali halides are in good agreement with the experimental values [5]. The value of $r(T)$ for every alkali halides computed by expression [eq. (7)] is slightly lower than computed values by eq. (8) for the entire range of temperatures because of the assumptions (*a* and *b*) which are used to develop eqs. (7) and (8). At melting temperature T_m of some of the ionic solids, the calculated value of $r(T_m)$ by using eqs. (7) and (8), show significant difference with the experimental data. The values of bulk modulus $B_T(T)$ are computed by using eqs. (10) and (11) for the entire range of temperatures. A comparison

is presented in Table 2(a–d) for the case of NaCl. The experimental data for NaCl [26] are available. The calculated and experimental values are found to be in good agreement with each other. In case of LiF also, we have good agreements with experimental and calculated values above and below Debye temperature.

Table 2(a). Calculated value of interatomic separation $r(T)$ in Å and bulk modulus $B_T(T)$ in unit of ($\times 10^{-1}$) GPa at different temperature. The experimental data are taken from [5,25].

	LiF						NaCl					
	$r(T)$			$B_T(T)$			$r(T)$			$B_T(T)$		
	Eq.7	Eq.8	Exp.	Eq.10	Eq.11	Exp.	Eq.7	Eq.8	Exp.	Eq.10	Eq.11	Exp.
300	2.013	2.013	2.012	665.0	665.0	665.0	2.820	2.820	2.820	240.0	240.0	240.0
400	2.020	2.020	2.019	624.1	624.1		2.832	2.832	2.831	223.0	223.0	224.1
500	2.027	2.027	2.028	583.3	585.2		2.844	2.844	2.845	206.0	205.9	205.0
600	2.035	2.035	2.037	542.4	542.3		2.858	2.858	2.860	189.0	188.9	188.0
700	2.044	2.044	2.047	501.6	501.2		2.873	2.873	2.877	172.0	171.8	174.0
800	2.053	2.054	2.058	460.7	459.9		2.890	2.890	2.894	155.0	154.6	156.0
T_m	2.094	2.096	2.101	320.6	315.5		2.942	2.945	2.945	112.6	110.5	119.0

Table 2(b).

	KCl						KBr					
	$r(T)$			$B_T(T)$			$r(T)$			$B_T(T)$		
	Eq.7	Eq.8	Exp.	Eq.10	Eq.11	Exp	Eq.7	Eq.8	Exp.	Eq.10	Eq.11	Exp.
300	3.146	3.146	3.146	175.0	175.0	175.0	3.289	3.289	3.289	148.0	148.0	148.0
400	3.158	3.158	3.158	162.8	162.8		3.302	3.302	3.302	137.9	137.9	
500	3.171	3.171	3.170	150.6	150.6		3.317	3.317	3.316	127.8	127.8	
600	3.184	3.186	3.185	138.4	138.3		3.332	3.332	3.331	117.7	117.7	
700	3.201	3.203	3.200	126.1	126.0		3.349	3.349	3.346	107.6	107.3	
800	3.218	3.219	3.220	113.9	113.6		3.368	3.368	3.364	97.5	97.3	
T_m	3.270	3.273	3.259	84.2	82.9		3.413	3.416	3.401	77.0	76.1	

Table 2(c).

	KI						RbCl					
	$r(T)$			$B_T(T)$			$r(T)$			$B_T(T)$		
	Eq.7	Eq.8	Exp.	Eq.10	Eq.11	Exp	Eq.7	Eq.8	Exp.	Eq.10	Eq.11	Exp.
300	3.525	3.525	3.525	117.0	117.0	117.0	3.291	3.291	3.291	156.0	156.0	156.0
400	3.540	3.540	3.540	108.6	108.6		3.303	3.303	3.302	145.2	145.2	
500	3.556	3.556	3.556	100.2	100.2		3.315	3.315	3.316	134.4	134.4	
600	3.574	3.574	3.578	91.8	91.8		3.329	3.329	3.331	123.6	123.5	
700	3.594	3.594	3.592	83.4	83.3		3.344	3.346	3.346	112.8	112.6	
800	3.616	3.616	3.612	75.1	74.8		3.361	3.362	3.364	101.9	101.7	
T_m	3.656	3.658	3.646	61.9	61.2		3.399	3.400	3.399	81.4	80.6	

Table 2(d).

	RbBr						RbI					
	$r(T)$			$B_T(T)$			$r(T)$			$B_T(T)$		
	Eq.7	Eq.8	Exp	Eq.10	Eq.11	Exp.	Eq.7	Eq.8	Exp.	Eq.10	Eq.11	Exp.
300	3.445	3.445	3.442	132.0	132.0	132.0	3.668	3.668	3.668	105.0	105.0	105.0
400	3.458	3.458	3.457	122.5	122.5		3.684	3.684	3.683	96.7	96.7	
500	3.472	3.472	3.472	113.1	113.1		3.701	3.701	3.699	88.1	88.1	
600	3.487	3.487	3.487	103.6	103.6		3.720	3.720	3.716	79.7	79.7	
700	3.504	3.504	3.502	94.1	94.0		3.741	3.742	3.734	71.3	71.1	
800	3.523	3.523	3.518	84.7	84.4		3.765	3.766	3.753	62.8	62.5	
T_m	3.555	3.557	3.544	70.5	69.9		3.797	3.799	3.776	53.3	52.7	

To summarise, the assumption that the Anderson-Grüneisen parameter δ_T remains unchanged with temperature (T) above the Debye temperature (θ_D), leads to simple relations for finding the temperature dependent interionic separation and bulk modulus for alkali halides. For best explanation of interionic separation at melting temperature *i.e.*, $r(T_m)$ for ionic solids the Debye-Lindemann criterion of melting calculation may be useful and meaningful over the methods based on approximations (*a* and *b*). The good agreement between theory and experiment obtained in the present work confirms the internal consistency of thermodynamic relations from which most useful relations of temperature dependence of interionic separation and bulk modulus have been derived.

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